USE INFORMATION AND AIR MONITORING RECOMMENDATIONS FOR THE PESTICIDE ACTIVE INGREDIENTS SODIUM TETRATHIOCARBONATE

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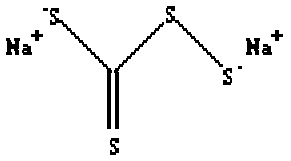
A. BACKGROUND

This recommendation contains general information regarding the physical-chemical properties of sodium tetrathiocarbonate and its reported historical uses as a pesticide in California. The Department of Pesticide Regulation (DPR) provides this information to assist the Air Resources Board (ARB) in their selection of appropriate locations for conducting pesticide air monitoring operations.

Physical-Chemical Properties

Figure 1. Chemical structure of sodium tetrathiocarbonate.



Sodium tetrathiocarbonate (Na_2CS_4) (Figure 1) has a vapor pressure of 25 mmHg at 24 ºC and is a deep amber liquid, pH 9.0, with a sulfurous smell (Unocal 1991f). It is stable at normal to high temperatures when dry and is non-flammable and non-explosive. Table 1 lists physical-chemical properties of Na_2CS_4.

Sodium tetrathiocarbonate is 100% soluble in water and degrades rapidly into carbon disulfide (CS_2) and hydrogen sulfide (H_2S). Hydrolysis is therefore a major environmental fate process. Short hydrolysis half-lives indicate that Na_2CS_4 does not persist long (Unocal 1991c1). Exposure to light will also cause fairly rapid degradation of Na_2CS_4, as photolysis half-lives range from 3 to 32 h (Unocal 1991c2). Thiosulfate, elemental sulfur, 1,2,4 trithiolane, and carbonate are produced from photolytic reactions. The soil adsorption coefficient is low—0.43 to 0.61—thus Na_2CS_4 is not likely to move with soil or contaminate groundwater. In addition, the emission potential calculated after thermogravimetric analysis was 0.0%, indicating that it does not contribute to ground-level ozone formation (Entek 1995). Toxicity to birds, fish and mammals is relatively low, with bobwhite quail and mallard duck dietary LC_{50} (5 d) greater than 5620ppm, rainbow trout acute LC_{50} at 6.7 mg/L, and rat acute inhalation LC_{50} (4 h) at 4.04 mg/L (Unocal 1991b1, 1991b2, 1991b3, 1991e).

Carbon disulfide is the actual biocidal agent and is always present in the environment, both through natural and anthropogenic sources. Consequently there is a high probability of exposure, but CS_2 is toxic to non-target organisms only at high concentrations. With a half-life of 1.1 years, hydrolysis is not a significant route of dissipation (Peyton et al. 1976). If CS_2 is released to the soil, it may have moderate mobility due to a K_{oc} value of 270 (HSDB 2006). However, contamination of groundwater is unlikely based on DPR monitoring results (DPR Well Inventory Database). Volatilization from moist soil and water surfaces are the most important fate processes for CS_2, and its vapor pressure of 294 mmHg at 20 °C suggests that it will exist as vapor in the atmosphere (Unocal 1991a).

Table 1. Physical and chemical properties of sodium tetrathiocarbonate.

Chemical name	sodium tetrathiocarbonate
Trade names[†]	Enzone, GY-81, ETK-1101
CAS Registry number	7345-69-9
Molecular formula	Na_2CS_4
Molecular Weight	186 g/mol[a]
Melting Point	N/A (liquid at room temperature)[a]
Boiling Point	101 ºC[a]
Specific Gravity	1.26 (21 ºC)[a]
Vapor Pressure	25 mmHg (24 ºC)[a]
Water Solubility	100%[a]
Henry's Law Constant	N/A (inorganic and polar)[a]
Soil Adsorption Coefficient (K_{oc})	0.43 – 0.61[b]
Octanol / Water Partition Coefficient (K_{ow})	N/A (inorganic and polar)[a]
Hydrolysis half lives	1 – 25 h (23 ºC)[c]
Photolysis half lives	3 – 32 h (25 ºC)[d]

[a]Unocal 1991f, [b]Unocal 1991d, [c]Unocal 1991c1, [d]Unocal 1991c2

B. CHEMICAL USES IN CALIFORNIA

Entek Corporation currently registers two products containing Na_2CS_4—Enzone and ETK-1101. ETK-1101 contains a higher percentage of Na_2CS_4 than Enzone (53% versus 31.8%). These products are soil fumigants used as pre-plant, post-plant, or post harvest pesticides to control nematodes, insects, and plant pathogens (DPR Product/Label Database http://www.cdpr.ca.gov/docs/label/prodnam.htm). They are not restricted use pesticides (Entek 1999).

[†]Disclaimer: The mention of commercial products, their source, or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.

According to the label for Enzone, the pesticide is applied via irrigation systems in vineyards or almond, peach, plum, prune, orange, grapefruit, and lemon orchards. It is most commonly used to control grape phylloxera, nematodes, phytopthora root rot, and oak root fungus. Treatments cannot begin until the soil is 58 °F at 6 inches deep. Pre-irrigation prior to application is recommended for optimal penetration of the chemical into the soil. Between 250 and 2400 ppm active ingredient (a.i.) for 6 to 12 hours may be applied based on irrigation method and time of use (pre-plant vs. post-plant). If the air temperature is above 90 °F for 5 hours on the day of application, crop injury may result. Therefore, it is advisable to apply the lowest concentration of Na_2CS_4 from the recommended range.

There has been no reported use of ETK-1101 for the past five years, thus the only source of Na_2CS_4 in California was Enzone (DPR PUR Database, data for 2005 are preliminary). Total annual use of Na_2CS_4 ranged from 212,308 pounds in 2003 to 375,487 pounds in 2001 (Table 2). The top 11 counties overall, based upon pounds a.i. applied for each year, are represented in Table 2; monthly use in the top 3 counties are shown in Table 3. Kern, Tulare, and Monterey counties had the highest usage in all years except 2004, when Monterey County ranked fourth after Kern, Madera, and Tulare counties. The greatest amount of pounds a.i. applied in Kern and Tulare counties occurred in March, April, May, September, October, and November. Peak use in Monterey County occurred in May, June, July, and November. The six commodities overall receiving the most Na_2CS_4 were grapes, wine grapes, lemon, peach, almond, and prune; combining the use on all grapes accounts for 88% of the total pounds of Na_2CS_4 applied (Table 4).

Table 2. Annual Na_2CS_4 Use by the Top 11 Counties Overall (Pounds Active Ingredient)

COUNTY	2001	2002	2003	2004	2005	TOTAL
KERN	80851	137848	108614	108569	147737	583619
MADERA	11437	23893	11289	34842	0	81460
MENDOCINO	2329	3946	1736	1316	3172	12499
MERCED	34076	0	687	0	4108	38871
MONTEREY	91830	31709	28739	25577	29623	207478
RIVERSIDE	0	1430	0	16993	7057	25480
SAN JOAQUIN	19851	10985	6739	16657	0	54231
SAN LUIS OBISPO	14665	14673	615	0	0	29953
SANTA CLARA	12176	14629	2438	11253	8660	49156
TULARE	80518	66174	29737	28014	28457	232900
VENTURA	7360	23283	9387	1398	4260	45688
Total for Top 11 Counties	355093	328569	199981	244618	233074	1361335
Percent of CA Total	95	93	94	94	71	89
Total Statewide Use	375487	352342	212308	259542	329678	1528722

Table 3. Monthly Agricultural Na_2CS_4 Use by the Top 3 Counties (2001 – 2005)
(Pounds Active Ingredient)

COUNTY / YEAR		JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEPT	OCT	NOV	DEC	TOTAL
Kern	2001	0	0	0	37654	5369	6674	10223	0	3925	0	17006	0	80851
	2002	0	1589	11748	37811	20927	0	2398	0	10587	43847	8941	0	137848
	2003	0	0	12085	16551	13084	7852	0	0	23017	14686	18535	2803	108614
	2004	0	0	20493	36117	1500	69	0	0	30506	17483	2400	0	108569
	2005	0	0	3535	20604	23082	6609	1430	0	45045	14940	29632	2861	147737
Total		**0**	**1589**	**47861**	**148737**	**63962**	**21204**	**14051**	**0**	**113080**	**90956**	**76514**	**5664**	**583618**
Tulare	2001	0	0	0	28550	24382	1357	3772	0	286	4127	18045	0	80519
	2002	0	0	0	14149	8471	7955	4116	0	0	12505	18977	0	66173
	2003	0	0	19864	2893	1429	1179	0	0	0	0	4372	0	29737
	2004	0	0	0	22394	1017	4603	0	0	0	0	0	0	28014
	2005	0	0	0	5289	0	11830	865	0	0	1202	9272	0	28457
Total		**0**	**0**	**19864**	**73275**	**35299**	**26924**	**8753**	**0**	**286**	**17834**	**50666**	**0**	**232901**
Monterey	2001	0	0	0	0	28374	24106	13860	13942	0	0	11547	0	91829
	2002	0	0	0	0	3814	20879	2801	0	0	0	3682	534	31710
	2003	0	0	0	0	2193	22972	1326	0	0	0	2247	0	28738
	2004	0	0	0	9250	2359	11609	0	0	0	0	2359	0	25577
	2005	0	0	0	2902	4654	6706	14144	0	0	0	1216	0	29622
Total		**0**	**0**	**0**	**12152**	**41394**	**86272**	**32131**	**13942**	**0**	**0**	**21051**	**534**	**207476**

Table 4. Annual Cropland Use of Sodium Tetrathiocarbonate by Top 6 Commodities.
(Pounds of Active Ingredient)

CROP	2001	2002	2003	2004	2005	Total
GRAPES	183486	199213	130124	195555	136780	845158
GRAPES, WINE	175976	115654	64593	54599	90024	500846
LEMON	6934	19556	8554	1398	4997	40803
PEACH	2889	326	1775	3719	3711	12420
ALMOND	2205	5391	0	3519	90171	101286
PRUNE	0	703	4245	0	0	4947
Total for Top 6 Commodities	371491	340842	209289	258790	325683	1506095
Percent of CA Total	99	97	99	100	99	98
Total Statewide Use	375487	352342	212308	259542	329678	1529357
Total for Grapes and Grapes, Wine	359463	314867	194716	250154	226804	1346004
Percent of CA Total	96	89	92	96	69	88

C. APPLICATION SITE AIR MONITORING RECOMMENDATIONS

Due to the immediate degradation of Na_2CS_4 into H_2S and CS_2 upon dilution in water as well as the biocidal nature of CS_2, DPR recommends application-site monitoring for CS_2 and H_2S. Based on a preliminary assessment of the toxicology data, the target quantitation limit for CS_2

should be 0.5 µg/m^3. The Jerome hydrogen sulfide Analyzer takes an instantaneous reading with a detection limit of 3 ppb.

Growers in Kern County used the most Na_2CS_4 in all years except 2001, when use was second to Monterey County. The majority of applications in Kern County occurred during the spring and fall. These applications were primarily used to treat vineyards; grapes received on average 99% of the treatments between 2001 and 2005. Therefore, DPR recommends that monitoring occur in a vineyard in Kern County either in spring or fall. Figures 2 – 4 show use amounts and locations in Kern County during Spring 2003, 2004, and 2005. Figures 5 – 7 show use amounts and locations during Fall 2003, 2004, and 2005.

According to the product label for Enzone, 700 – 1450 ppm a.i. should be applied to established vineyards via drip irrigation at 5 – 30 gal/acre/treatment for up to 8 hours. For flood and furrow irrigation, 250 – 500 ppm a.i. should be applied at 20 – 30 gal/acre/treatment for up to 6 hours. DPR requests that ARB monitor a flood or furrow application at the highest allowed rates of use (500 ppm a.i. for an established vineyard or 950 ppm a.i. as a preplant application).

Vineyard sites ranged from 10 to 293 acres treated, with an average for 2001 through 2005 of 69 acres (DPR PUR Database, data from 2005 are preliminary). However, entries in the PUR database may reflect multiple applications of the same site, resulting in high reported acreage. DPR therefore recommends that the selected monitoring site be 69 to 264 acres. If a site this size cannot be located, a smaller site is acceptable. A minimum of eight samplers should be positioned around the application site, one on each side of the site and one at each corner. A ninth replicate sampler should be co-located at one position. Ideally, samplers should be placed a minimum of 20 meters from the application area. DPR recommends coordination with the county agricultural commissioner to select the most appropriate sampling sites. If a site is located on a private property, permission from the property owner must be obtained. Air samples should be taken before, during, and after application and for three Daytime/Overnight sampling periods as in the following schedule.

Sample period begins:	**Sample duration time**
Background (pre-application)	Minimum 12 – 24 hours
Application	Start of application until 1 hour before sunset
1 hour before sunset (post-application)	Overnight[1] until 1 hour after sunrise
1 hour after sunrise	Daytime until 1 hour before sunset
1 hour before sunset	Overnight until 1 hour after sunrise
1 hour after sunrise	Daytime until 1 hour before sunset
1 hour before sunset	Overnight until 1 hour after sunrise

[1]All overnight samples must include the period from one hour before sunset to one hour after sunrise.

Hydrogen sulfide readings will be collected at each CS_2 sample change over time at each sampling site.

Field spikes for carbon disulfide and trip blanks should be prepared in the laboratory and run in the field with the samples for quality assurance.

DPR requests the following information be included in the monitoring report:

1) an accurate record of the application site, including topographic features

2) an accurate record of the positions of the monitoring equipment with respect to the application site, including the exact direction and distance of the samplers from the edge of the application site

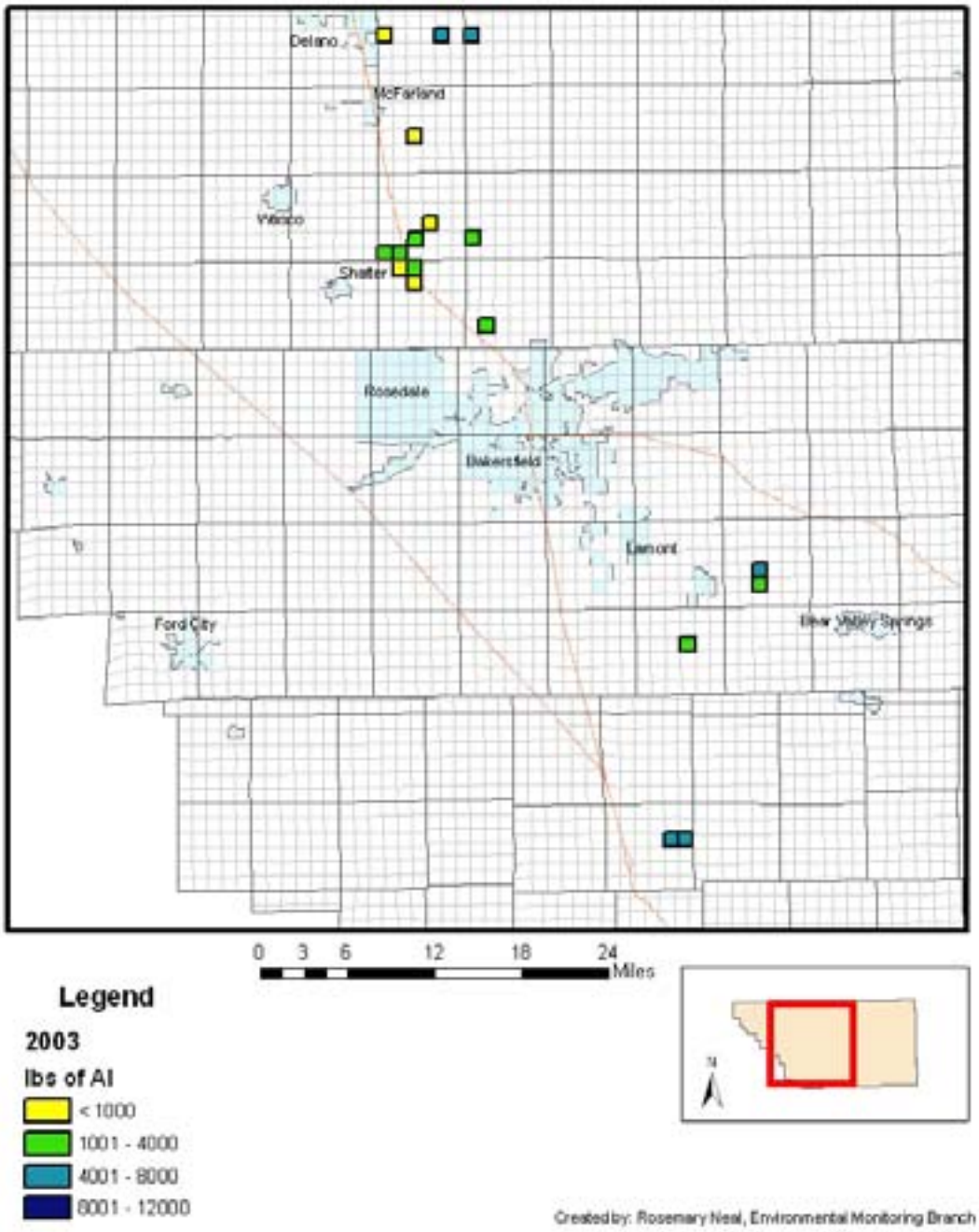
3) an accurate record of pesticide application, including application dosage or quantity of pesticide applied, application starting and ending time, method and application rate, etc.

4) an accurate drawing of the monitoring site showing the precise location of the meteorological equipment, trees, buildings, and other obstacles with respect to North (identified as either true or magnetic North)

5) if applicable, meteorological data collected at 1-minute intervals including wind speed and direction, humidity, air temperature, and comments regarding degree of cloud cover.

Figure 2

Kern County
Sodium Tetrathiocarbonate Use
Spring 2003



Created by: Rosemary Neal, Environmental Monitoring Branch

Figure 3

Kern County
Sodium Tetrathiocarbonate Use
Spring 2004

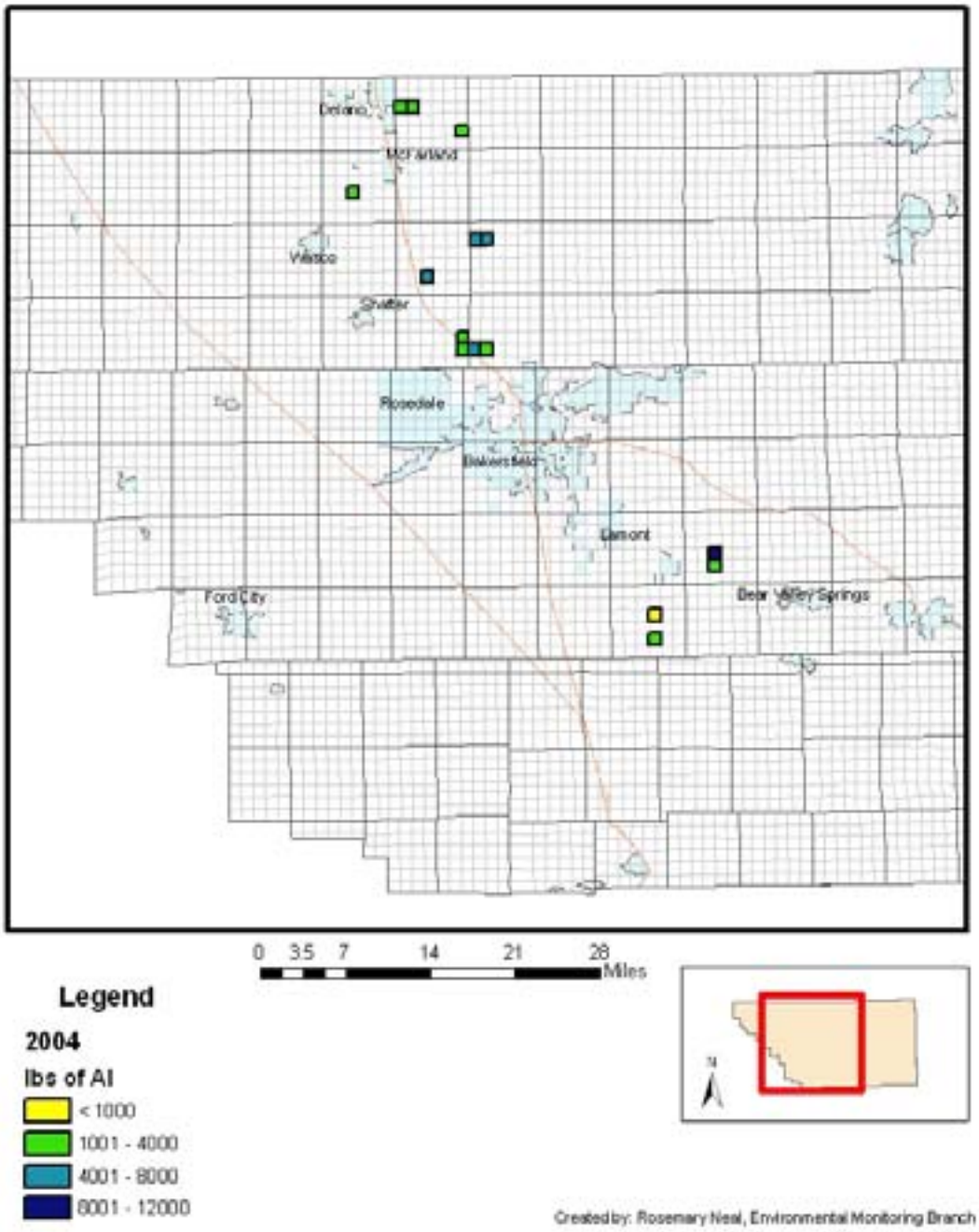


Figure 4

Kern County
Sodium Tetrathiocarbonate Use
Spring 2005

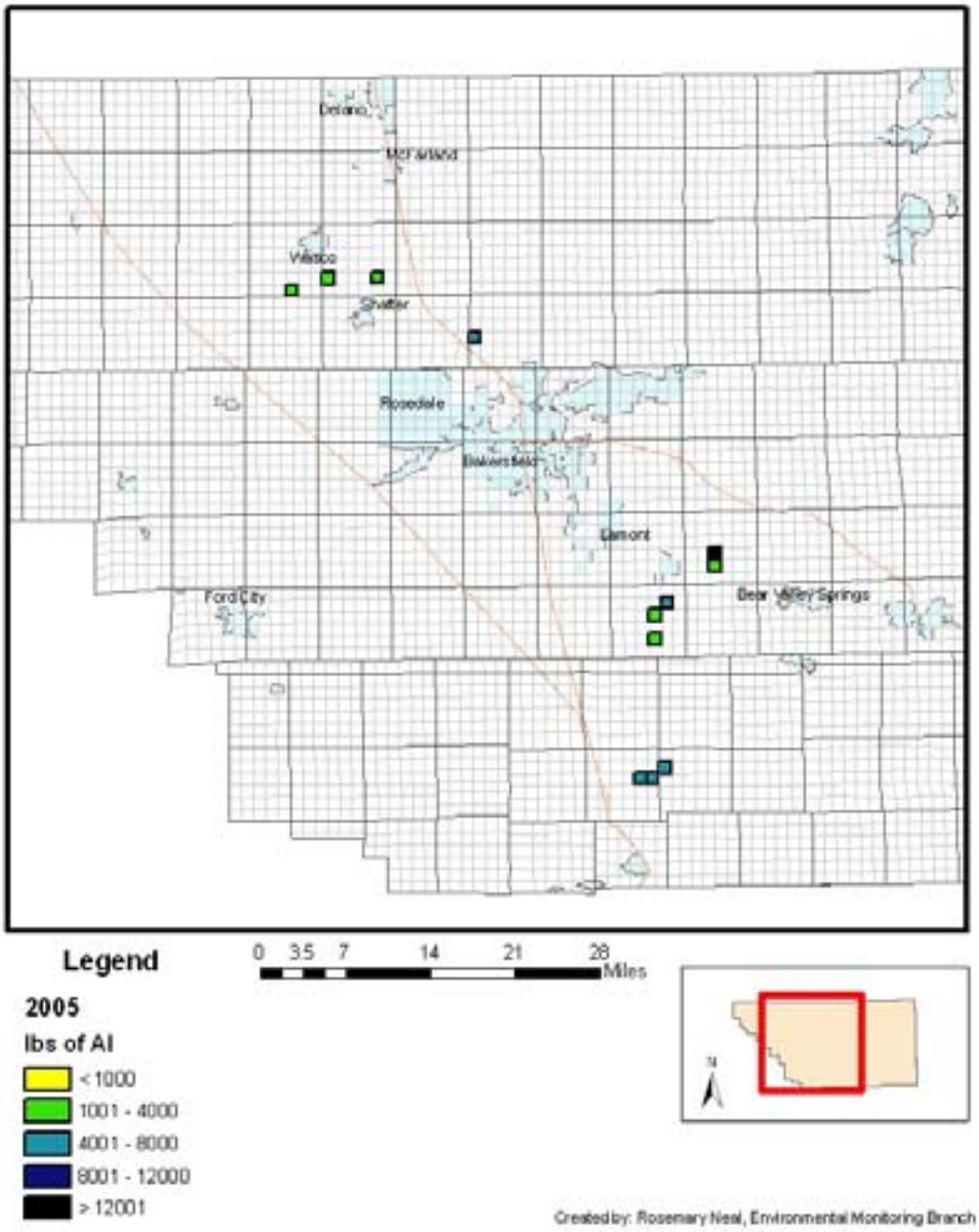


Figure 5

Kern County
Sodium Tetrathiocarbonate Use
Fall 2003

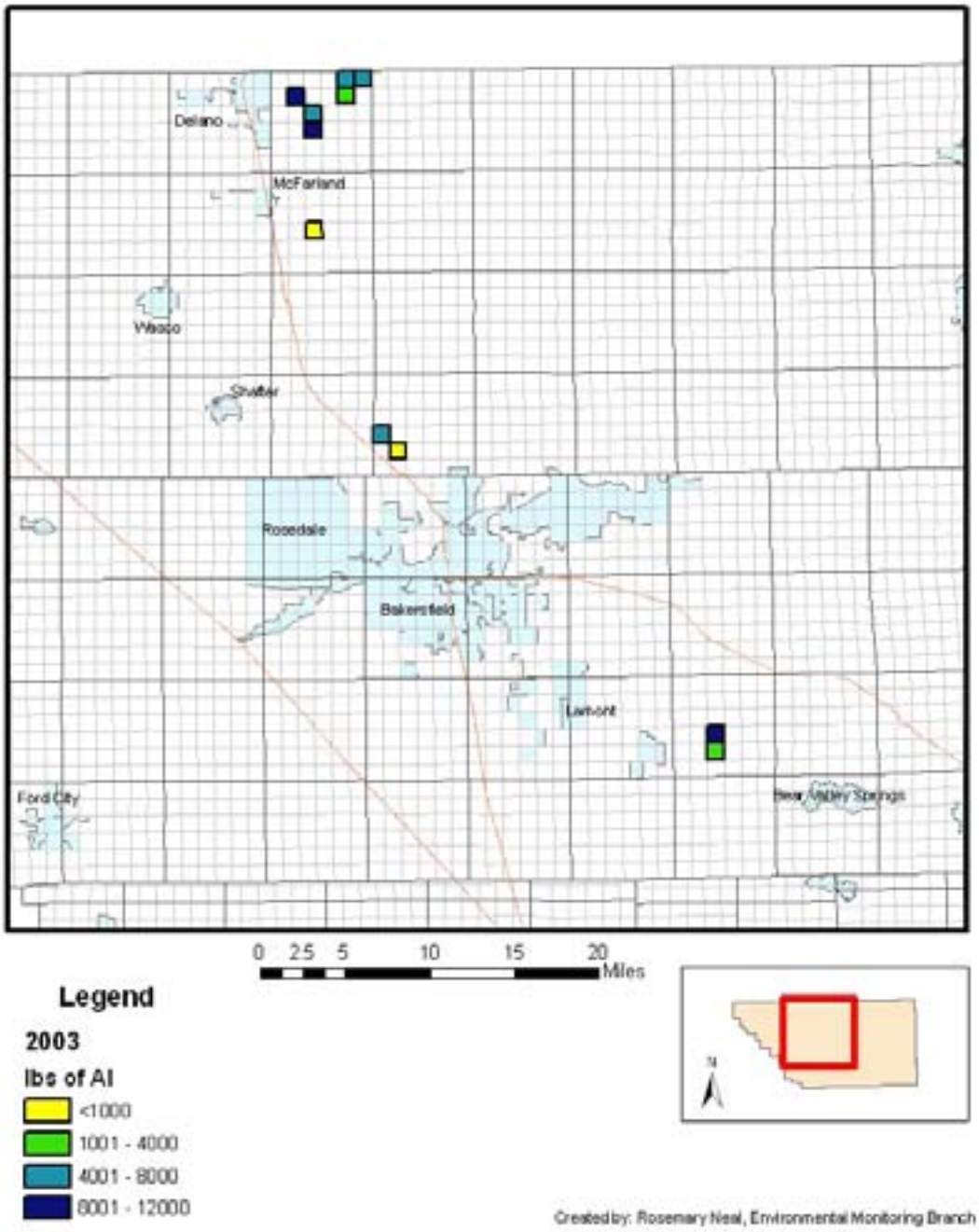


Figure 6

Kern County
Sodium Tetrathiocarbonate Use
Fall 2004

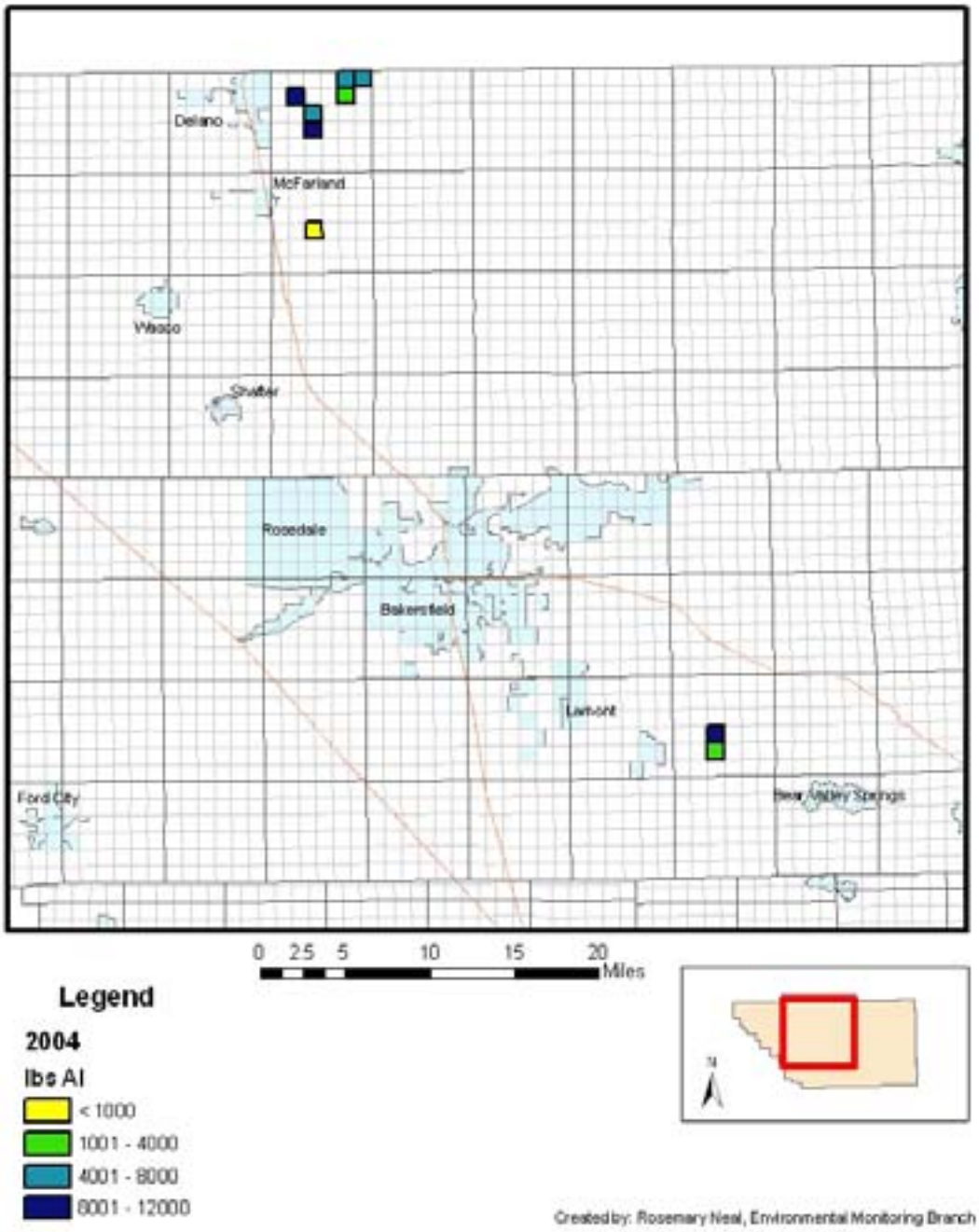
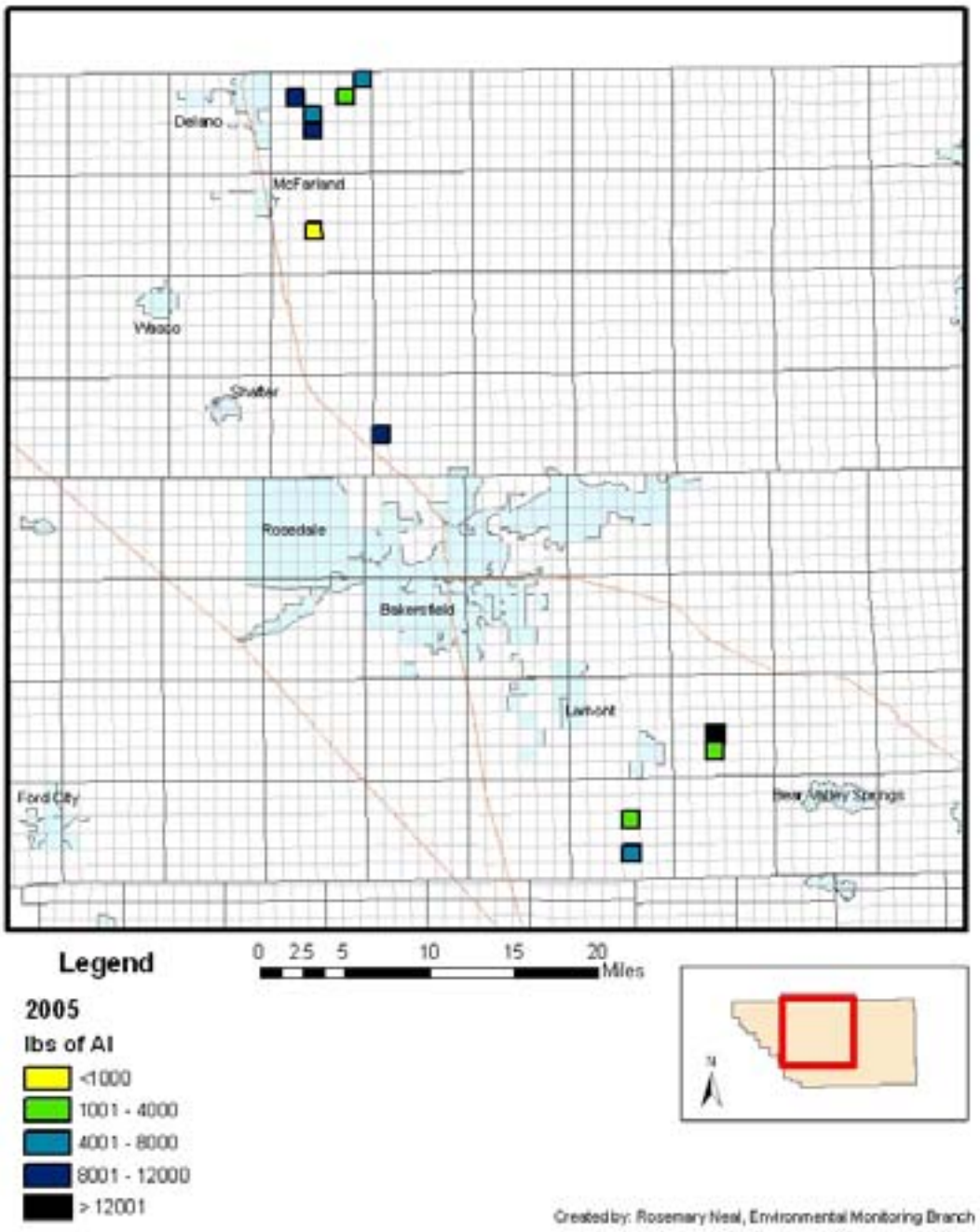


Figure 7

Kern County
Sodium Tetrathiocarbonate Use
Fall 2005



D. SAFETY RECOMMENDATIONS

The product label for Enzone carries a danger warning. The pesticide is corrosive and harmful if inhaled. Applicators and handlers must wear coveralls over long-sleeved shirts and pants, socks with chemical-resistant footwear, waterproof gloves, protective eyewear, and respirators with organic-vapor-removing cartridges with pre-filters approved for pesticides. Any protective equipment heavily contaminated with the pesticide should be discarded, otherwise it should be cleaned and washed after use. Re-entry period for any person other than applicators and handlers is four days.

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